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Preconcentration of Gadolinium Ion by Solidification of Floating Organic Drop Microextraction and Its Determination by UV-Vis Spectrophotometry

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ABSTRACT

A solidified floating organic drop microextraction (SFODME) combined with UV-Vis spectrophotometry was applied for preconcentration and determination of Gd(III). In this study, Morin (3, 5, 7. 2′, 4′ pentahydroxy flavone) as a suitable ligand and 1-Dodecanol as extraction solvent were used. Following the extraction Gd-Morin complex, the extraction solvent was transported to a spectrophotometer for determination of Gadolinium ion at the absorption wave length of 440 nm. The main affecting factors in the performance of SFODME such as pH, concentration of Morin, extraction time, stirring rate and sample volume were investigated and optimized. Under the optimum conditions, the enrichment factor of 23, linear dynamic range of 80-900 μg L^{-1} with correlation of determination (R^2>% 99) and limit of detection of 172μg L^{-1} were obtained for determination of Gd(III). The relative standard deviation (n = 5) for 150 μg L^{-1} of Gd(III) (sample volume 4.0mL) was ±2.17%. The method was successfully applied for preconcentration and determination of Gd(III) in water samples.

Keywords: solidified floating organic drop microextraction, UV-Vis spectrophotometry, Gadolinium, Morin

INTRODUCTION

Gadolinium is a silvery-white malleable and applied extensively in color TV tubes, manufacturing compact discs and computer memories, energy-saving lamps and glasses [1]. This element can rarely be found in nature in two different kinds of ores such as monazite and bastnasite [2].

There are many methods available for determination of rare earths in various samples such as environment, industry, geology, clinical and etc. [3]. Different analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) [4-8], electron spin resonance (ESR) [9, 10], spectrofluorometry [11, 12], electrochemical sensor [13, 14, 2, 15, 16] and neutron activation analysis [17] have been performed to determine Gadolinium in various samples. Usage of spectrophotometry for determination of Gd(III) is very suitable because this method is the inexpensive and available in all laboratories. The most important problem for measuring Gd(III) with spectrophotometry in real samples is the presence of interfering species and matrix effects. Therefore, a sample preparation procedure is necessary for reducing matrix effects and to concentrate the Gadolinium ion before analysis.

Sample preparation is an important step for determination of analytes in real samples and successful measurement of analyte depends on this method. Microextraction method as a sample preparation procedure is used for extraction, purification and concentration of volatile, non-volatile, polar, non-polar, ionic and metallic

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analytes from various real samples [18]. In early 1990, solid-phase microextraction (SPME) was produced. SPME is a rapid, simple, solvent free, cost effective and sensitive method [19]. Important disadvantages of SPME are fiber breakage and stripping of coatings. In order to overcome these problems, liquid-phase microextraction (LPME) was introduced. Nowadays, a new mode of LPME named solidification of floating drop microextraction (SFDME) has been developed. In this method, a small amount of a water-immiscible solvent (as acceptor phase) with melting point near to room temperature (10-30°C) is delivered to the surface of water sample solution containing analyte, and solution is stirred for a desired time. The sample vial is then cooled by inserting sample vial into an ice bath and the solidified organic solvent is transferred into a suitable vial and the melted organic solvent is finally used for analyte determination [20, 21]. Furthermore, the SFODME has the advantages of simplicity, short extraction time, low cost, minimum organic solvent consumption and high enrichment factor [22-24].

In the present study, SFODME combined with UV-Vis spectrophotometry was applied for preconcentration and determination of trace amount of Gadolinium ion in real water samples. In order to transfer Gadolinium ion into an organic solvent as accepter phase, Morin was selected as a ligand to form a suitable complex with Gd(III) ion in presence of various species [25]. Moreover, it is also a green ligand and environmental friendly [26-28]. The effect of different species in the extraction and determination of Gd(III) were studied and showed that the most ions have no significant interference effects. The main influencing factors in the extraction efficiency such as pH of sample solution, amount of ligand, extraction time, stirring rate and salt addition were investigated and optimized. The proposed method was finally applied at the optimum conditions to determine Gd(III) in real water samples and the results indicated that the method is very suitable for analysis of Gd(III).

EXPERIMENTAL

Reagents

A stock standard Gadolinium (III) solution (3000mgL^{-1}) was prepared by dissolving 0.1320g Gd (No3)$_3$.6H$_2$o (Merck, Darmstadt, Germany) in ultrapure water. Morin (3, 5, 7. 2′, 4′ pentahydroxy flavone) was obtained from Merck and working solution (1000mg L^{-1}) was prepared by dissolving appropriate amounts of this reagent in methanol (Merck). 1-dodecanol (Sigma, Alderich) was used as accepter phase for the microextraction method. Prior to commencement, the pH of solution was adjusted with (0.01mol L^{-1}) hydrochloric acid and sodium hydroxide solutions.

Instrumentation

The analysis was performed using Varian UV-Vis spectrophotometry, Model Carry 50 Bio equipped with Xe lamp and quartz microcell (0.2 and 0.1 ml). pH of sample solution was measured by a pH-meter Metrohm 780. A magnetic heater-stirrer (Yellow line, USA) was used for stirring of the sample solution. A Transferprtte micro-sampler (Germany) was applied for handling Morin and 1-dodecanol.

SFODME procedure for determination of Gadolinium

First, 4.0 ml of the standard solution containing 150µgL^{-1}of Gadolinium ion was transferred into a screw caped vial followed by addition of 2.0 mL of Morin solution (12mgL^{-1}). The pH of sample solution was then adjusted at 7.0 with (0.01mol L^{-1}) hydrochloric acid and sodium hydroxide solution. 200µL of 1-dodecanol was placed on the surface of the sample solution by an auto sampler and the sample solution was stirred for 15 min at 800 rpm to form the Gd(III)-Morin complex and transfers into the accepter phase. After the extraction of the complex, the vial was placed in water-ice bath at 0^{oC} for 6 minutes. The solidified solvent was immediately transferred to a conical vial by a mini-spatula where it was rapidly melted. Subsequently, the resultant accepter phase (organic solvent) was transferred to spectrophotometer for determination of Gadolinium ion at the absorption wavelength of 440 nm.

RESULTS AND DISCUSSION

Study on the Absorption Spectrum of Complex

In this work, UV-Vis spectrophotometry was applied to determine the Gd-Morin complex. In order to carry out the quantification analysis of Gd, the wavelengths of maximum absorption for Gd(III)-Morin complex and Morin were obtained. In the preliminary experiment, absorption curves were measured for Morin and Gd-Morin complex in the range of 200 nm-600 nm. During determination, the blank absorbance of reagent was corrected and the results are shown in **Figure 1**. The absorption wavelengths of 265 and 395 nm were obtained for Morin, and the wavelengths of 271and 440 nm were obtained for the Gd-Morin complex. The results indicated that the maximum

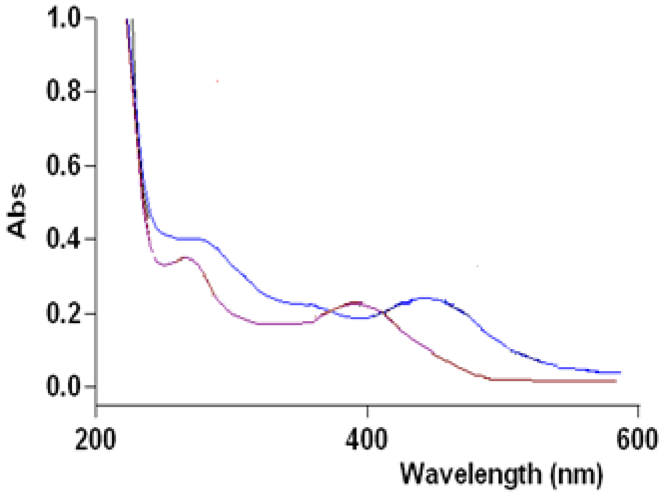

Figure 1. Morin (red curve) and Gd-Morin complex after the SFODME (blue curve).
Extraction conditions: water sample volume, 2.0ml; amount of amount of Gd(III), 150 μg L^{-1}; organic solvent volume, 200μl; Morin solution volume, 2.0 mL; extraction time,15min.

absorption wavelengths after extraction moved towards long wavelengths (red shift). Because of the low peak shift at a wavelength of 261nm, it cannot be used to measure the Gd-Morin complex because the ligand and the complex both are absorbed at this wavelength. Moreover, the maximum absorption wavelength of 440 nm showed higher sensitivity for spectrophotometric determination of the Gd-Morin complex. Therefore, the absorption wavelength of 440 nm was selected as the working wavelength for further analysis.

Effect of SFODME Parameters

Effect of pH

Neutral Complex or ion pairs can be easily extracted into the organic solvent. Therefore, the extraction of metal ions by SFODME involves complex formation or ion pairs with sufficient hydrophobicity [29]. It is clear that the complex formation in aqueous solutions is pH dependent thus; pH of the sample solution is an important factor to reach high extraction efficiency. Choosing proper pH can help to create the perfect interaction between the ligand and the analyte and complex formation. Moreover, it can reduce the complex formation between the ligand and interfering species, and matrix effects. Therefore, the effect of pH on the extraction of Gd(III) was studied in the pH range of 5-9. In order to adjust the pH of sample solution, hydrochloric acid and sodium hydroxide solutions (0.01molL^{-1}) were used. Each experiment was repeated three times and the mean of absorbance was used as a response. Trend of pH variation in the extraction of Gd(III) is presented in **Figure 2**. Consequently, an abrupt rise took place at pH of 5-7 and then moderately declined. Therefore, the extraction efficiency and complex formation was hardly increased with increasing of pH from 5 to 7 and then it gently decreased and reached to a constant value at higher pHs. Thus, pH of 7.0 was chosen for measurement of Gd(III) as the optimum value.

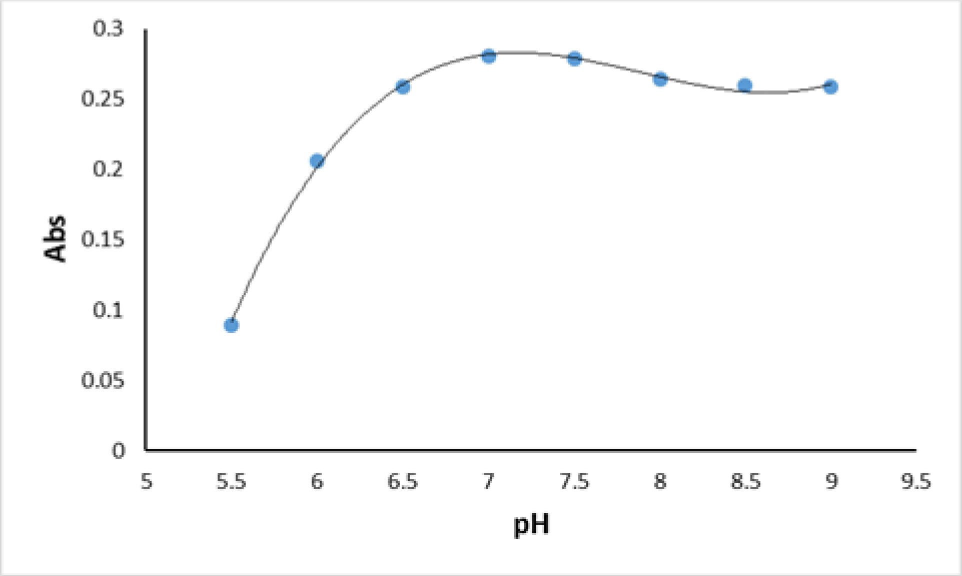

Figure 2. Effect of pH on extraction of Gd(III) by SFODME method (n=3).
Extraction conditions: water sample volume, 2.0mL; amount of amount of Gd (III), 150 μgL^{-1}; organic solvent volume,200μL; Morin solution volume, 2.0 mL; extraction time,15min.

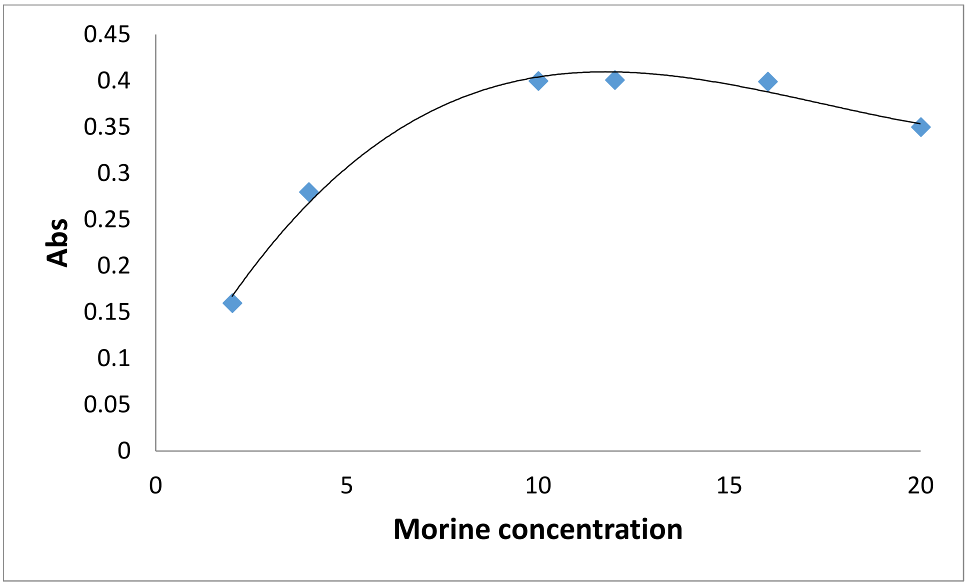

Figure 3. Effect of Morin concentration on extraction of Gd(III) by SFODME method (n=3).
Extraction conditions: water sample volume, 2.0mL; amount of Gd (III), 150 μgL^{-1}; organic solvent volume, 200μL; Morin solution volume, 2.0 mL; extraction time,15min.

Effect of Morin concentration

Complex formation is an equilibrium process and so increasing the ligand concentration for equilibrium shift towards the formation of a complex is effective. However, High concentrations of ligand in solution can increase the extraction cost of analyte and the probability of complex formation with interfering species. Therefore, optimization of ligand concentration is essential in the microextraction process. In order to study the influence of Morin concentration on the extraction efficiency of Gd(III), different concentrations of the Morin (2-20 mgL^{-1}) were used (**Figure 3**). It was found that the absorbance signal of Gd-Morin complex increased in parallel with the Morin concentration to 12 mgL^{-1} and decreased at higher concentrations of ligand which may be resulted from saturation of extracting solution. Therefore, Morin concentration of 12 mg L^{-1} was selected for subsequent analysis.

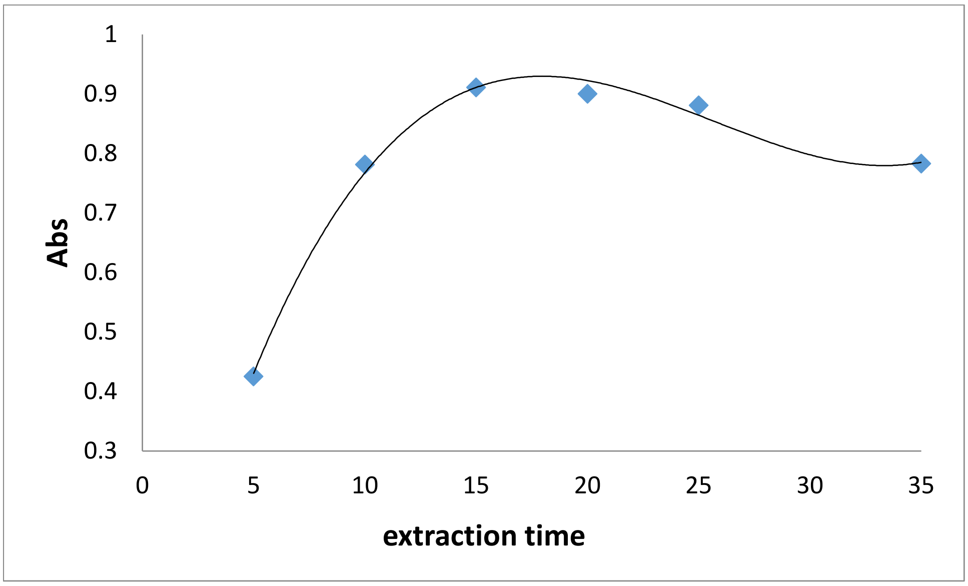

Figure 4. Effect of extraction time of Gd(III) by SFODME method (n=3).
Extraction conditions: water sample volume, 2.0mL; amount of amount of Gd (III), 150 µgL^{-1}; organic solvent volume, 200µL; Morin solution volume, 2.0 mL.

Effect of extraction time

Extraction time is an important factor in extraction procedures. In order to obtain a beneficial precision, sensitivity and speed, it is necessary to select an extraction time that guarantees the equilibrium between aqueous and organic phases, and maximum extraction of analyte [24]. It is clear that the complex concentration is constant after equilibrium time and does not change with increasing the time. Therefore, the effect of extraction time was examined with changing the time from 5 to 35 minutes at a stirring rate of 800 rpm. The results in **Figure 4** revealed that the extraction is quantitative (>95%) at 15 min, but a further increase in extraction time causes a slight decrease in extraction efficiency. Therefore, an extraction time of 15 minutes was selected for subsequent experiments.

Effect of salt addition

Several effects may take place when ionic strength of the solution increases. The presence of dissolved salt in water can change the physical properties of the Nernst diffusion film and reduces the rate of diffusion of the target analytes into the drop [30]. Adding salt often improves the extraction of analytes in SFODME due to the salting-out effect. In other hand, adding salt can reduce the complex solubility and assists to extract the complex into the organic phase. In order to verity the suitability of the method for determination of Gd(III), the effect of NaCl addition on the extraction was investigated by changing its concentration within the range of 0-1mol l^{-1}. The results showed that salt addition has no significant effect on the extraction efficiency. This might be due to the effect which is the opposite of salting-out and salting-in. Although the salting-out effect reduces the complex solubility in water but the salting-in effect increases the solubility with increasing the ionic strength of a solution. Therefore, all the extraction experiments were performed without adding any salt.

Effect of stirring rate

An important parameter which has a great effective in the extraction efficiency and the extraction time is the stirring rate. The stirring rate has a direct influence on the droplet properties and mass transfer characteristic in the aqueous sample [21]. Stirring the sample solution decreases the required time to achieve the equilibrium between the sample solution and the droplet by enhancing the diffusion of the analytes towards the organic phase [31]. The effect of stirring rate on the extraction efficiency of Gd(III) in the range of 300-1000 rpm was investigated. The results in **Figure 5** showed that the absorbance increased by increasing the stirring rate from 300 to 800 rpm, and then reduced at higher stirring rate up to 1000 rpm. Thus, a stirring rate of 800 rpm was selected in this study.

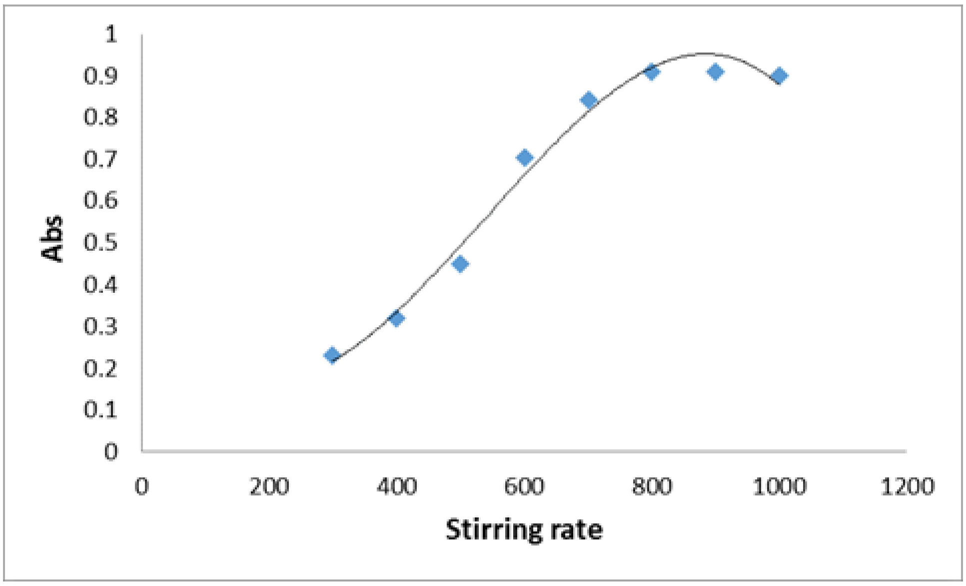

Figure 5. Effect of stirring rate on extraction of Gd(III) by SFODME method(n=3).
Extraction conditions: water sample volume, 2.0mL; amount of Gd (III), 150 μgL^{-1}; organic solvent volume, 200μL; Morin solution, 2.0 mL; extraction time,15min.

Effect of sample volume

In SFODME, sample volume is an important parameter that affects the extraction efficiency and preconcentration factor. The preconcentration factor is used to investigate the ability of microextraction method for concentration of analyte. This factor is directly proportional to the sample solution volume and inversely proportional to the acceptor phase volume and so it is increased with increasing of the ratio of the sample solution volume to the acceptor phase volume [32]. However, the preconcentration factor is independent with an infinitely volume of the sample solution. The effect of sample solution volume in ranges of 1-10mL on the extraction of Gd(III) was evaluated while the acceptor phase volume was kept constant. The results showed that the extraction was quantitative (recovery >95%) with the aqueous phase volume in the range of 2-4 ml, and decreased with further increase of sample volume. Thus, a sample volume of 4.0ml was used for all subsequent extractions.

Effect of Coexisting Ions

The effect of interference ions on the preconcentration and determination of analyte are investigated and the results are shown in **Table 1**. In order to study these effects, 4.0 ml of the 150 μg L^{-1} Gd(III) solution was subjected with 100 fold excess of interfering ions and the microextraction procedure was performed at the optimum conditions. The tolerance limit was defined as the concentration of added ion that caused less than ±5% relative error in the determination of Gd(III). **Table 1** represents the interferences of La^{3+}, Pb^{2+}, Cd^{2+}, Fe^{2+}, whereas other ions show no significant interference at the given level of interested metal ions.

Table 1. Effect of foreign ions on the extraction recovery of Gd(III) with SFODME method(n=3).
Condition: sample solution volume, 4.0ml; Gd (III) and foreign ions at a concentration of 150 μg L^{-1}and 15.0mgL^{-1}, respectively.

Foreign ions	Recovery (%)
Na^+	97.8
Cl^-	98.8
NO_3^-	99.3
CH_3COO^-	102.6
SO_3^{2-}	90.3
K^+	96.1
Cd^{2+}	87.2
Pb^{2+}	81.6
Cu^{2+}	95.6
Fe^{2+}	90.1
Co^{2+}	95.5
La^{3+}	129.5

Table 2. Results (mean ± standard deviation based on three replicate analysis) of determination of Gadolinium ion in real sample.

Sample	Spike (μg.l^{-1})	Found (μg.l^{-1})	Recovery (%)
Tap water [a]	0	ND[b]	-
	150	145.0 ± 0.5	96.7
	300	287.1 ±0 .6	95.7
River water[c]	0	ND	-
	150	142.1 ± 0.7	94.73
	300	312.5 ± 0.4	104.17

[a] Obtained from Mashhad [b] Not detected [c] Obtained from Torghabeh

Evaluation of Performance of the Method

The calibration graphs were linear in the range of 80-900 μgL^{-1} Gadolinium ion under the optimum conditions for the SFODME procedure. The regression equation for Gadolinium determination was A = 0.001 C -0.043, where A is the absorbance and C is the Gd ion concentration in solution (μgL^{-1}). The correlation coefficient of the calibration curve equation was 0.9931. The relative standard deviation (n = 5) for 150 μg L^{-1} of Gd(III) (sample volume 4.0mL) was± 2.17%. The limit of detection (LOD) was calculated as the ratio of three times of the standard deviation of blank signal to the slope of the calibration curve for extracting 4.0mL of water solution at pH 7.0 was 172μg L^{-1}. Enrichment factor was calculated as the slope ratio of two calibration curves after and before the preconcentration and was 23.

Analysis of Real Samples

In order to test the applicability of the proposed SFODME method for the analysis of real samples, tap and river water (obtained of Mashhad and Torghabeh) were studied. In order to remove each solid material, all water samples were centrifuged at 6000 rpm for 7min and was filtered with filter paper No.0.45 μm before use. The water samples were pretreated using SFODME method (section2.3) and determined by UV-Vis spectrophotometry. The extraction recoveries for the spiked samples were in the acceptable range of 94.7-104.2% (**Table 2**).

CONCLUSION

In the present study, SFODME combined with Uv-Vis spectrophotometry was applied for preconcentration and determination of Gd(III) in real water samples. Morin as suitable ligand was used to form complex with Gd(III) and to extract Gd(III) in1-dodecanol drop as an acceptor phase and to determine the resultant complex with spectrophotometric method. Simplicity of operation, low sample volume, low cost and high enrichment factor are some advantages of SFODME for Gd(III) analysis. Spectrophotometric instrumentation was also used to analyze Gd(III) because of its simplicity, cheapness and portability. This study indicated that the conventional spectrophotometer coupled with SFODME could be successfully applied to determine trace and ultra-trace of metal ions. The proposed method also demonstrated a high sensitivity and relatively desirable reproducibility for Gd(III) determination in aqueous samples.

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